



Selective catalytic reduction of NO_x on combined Fe- and Cu-zeolite monolithic catalysts: Sequential and dual layer configurations

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ABSTRACT

Iron and copper-based zeolites are effective catalysts for the lean selective catalytic reduction (SCR) of NO_x with NH₃. Cu-zeolites are more active at lower temperatures ($\leq 350^\circ\text{C}$) while Fe-zeolites are more active at higher temperatures ($\geq 400^\circ\text{C}$). The effectiveness of a catalytic system comprising Fe- and Cu-based zeolites was examined for the standard (NO + O₂ + NH₃) and fast (NO + NO₂ + NH₃) SCR reactions. Experiments carried out with in-house and commercial Fe- and Cu-zeolite monoliths of varying lengths quantified their relative SCR activities. The commercial Cu-zeolite achieved complete NO_x conversion for the standard SCR at 250°C while the commercial Fe-zeolite achieved high NO_x conversion at higher temperatures ($\geq 400^\circ\text{C}$) where it out-performed the Cu-zeolite. Subsequently, three configurations of combined Fe and Cu-zeolite catalysts were compared:

- “Sequential brick” catalyst comprising Fe-zeolite and Cu-zeolite monolith.
- “Mixed washcoat” catalyst comprising a washcoat layer having equal mass fractions of Fe- and Cu-zeolites.
- “Dual layer” catalyst comprising monolith coated with individual layers of Fe- and Cu-zeolites of different thicknesses and mass fractions.

The sequential brick design with Fe-zeolite brick followed by a Cu-zeolite brick gave a higher conversion than the Cu/Fe sequence of equal loadings with the Fe(33%)/Cu(67%) achieving the highest NO_x conversion over a wide range of temperatures. The mixed washcoat catalyst achieved NO_x conversion that was nearly an average of the individual Fe-only and Cu-only catalysts. The dual layer catalyst with a thin Fe-zeolite (33% of the total washcoat loading) layer on top of a thicker Cu-zeolite layer (67%) resulted in very high NO_x removal efficiencies over a wide temperature range for both the standard and fast SCR reactions. The performance of this dual-layer system was comparable to the series arrangement of Fe and Cu-bricks. The Cu-zeolite on Fe-zeolite dual layer catalyst was not nearly as effective for the same loadings. The Fe/Cu dual layer catalyst also exhibited superior performance for the fast SCR reaction. The results are interpreted in terms of the activities of each catalyst for SCR and ammonia oxidation. An assessment of the extent of washcoat diffusion limitations shows that the dual layer configuration is superior to the sequential brick configuration. The existence of an optimal loading distribution of the Fe- and Cu-zeolite catalysts as well as other intangible benefits of the dual layer SCR catalyst are discussed.

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1. Introduction

Diesel vehicles are highly efficient and economical in terms of fuel consumption compared to the gasoline vehicles. But as is the case of all lean combustion processes, the NO_x produced is difficult to eliminate due to the unreacted O₂ in the product stream. This fact, coupled with the increasingly stringent NO_x emissions from

diesel vehicles, has prompted the development of various catalytic aftertreatment technologies. The two main ones that have emerged are NO_x storage and reduction (NSR) and selective catalytic reduction (SCR). SCR is now the preferred technology to achieve the large NO_x reductions mandated for medium and heavy-duty vehicles while NSR holds promise for light-duty vehicles.

SCR utilizes a variety of different reductants to convert NO_x to N₂. Amongst these, NH₃ (or urea) is the reductant of choice because of the high NO_x conversions that can be achieved at high space velocities encountered in vehicle applications. While NH₃-based SCR was first commercialized in the 1980s for stationary applications, it was only commercialized for diesel vehicles

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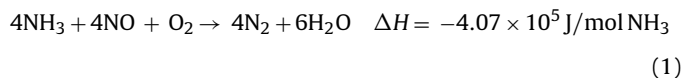
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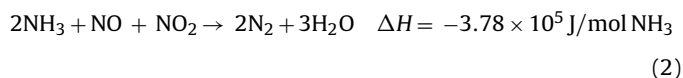
during the past decade. Various catalysts are being widely researched and used commercially for this purpose. Vanadia-based catalysts (e.g. $V_2O_5/WO_3/TiO_2$) are the most commonly used and widely investigated catalysts for SCR [1–5]. However, these catalysts have inadequate stability at the higher temperatures encountered in high load vehicle operation and are not suitable for systems including a particulate filter that actively regenerates at higher temperatures. Hence, the focus has shifted to Fe- and Cu-based zeolite catalysts, both of which have demonstrated very high NO_x reduction efficiencies at high space velocities. Cu-based catalysts are particularly effective at lower temperatures ($\leq 350^\circ C$) [6–9] which is desirable for vehicles that operate at low load for a large fraction of their use. Moreover, NO_x removal efficiencies on Cu-based catalysts are found to be rather insensitive to the amount of NO_2 in the feed at lower temperatures [6,10]. On the other hand, Fe-based catalysts are active at higher temperatures ($>350^\circ C$) and give very high NO_x reduction efficiencies even at very high temperatures (up to $600\text{--}700^\circ C$) [11–15]. The presence of feed NO_2 accelerates the NO_x conversion on Fe-zeolite catalysts, particularly at lower temperatures [6,12,13].

The catalytic reactions occurring during SCR have been extensively studied in the literature on the aforementioned vanadia, Fe-zeolite, and Cu-zeolite catalysts. There are three SCR reactions defined according to the composition of the feed NO_x ($NO + NO_2$). Each is catalyzed by either Fe- or Cu-zeolite materials and is highlighted as follows:

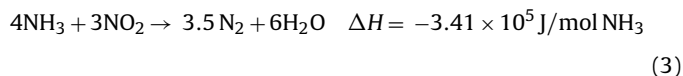
- **Standard SCR:** This reaction involves NO and NH_3 reacting in presence of O_2



- **Fast SCR:** This reaction is called the “fast SCR” reaction (2) because it has a much higher rate than the standard SCR reaction (1) due to the presence of NO_2 in the feed:

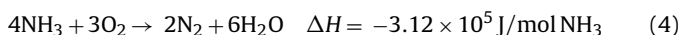


- **NO_2 SCR:** This overall reaction occurs when the feed NO_x consists of only NO_2 :



In our recent study [11], we showed that NO oxidation is the rate determining step for the standard SCR reaction on Fe-zeolite catalyst. A recent study by Luo et al. [16] used a modified FTIR method to spatially resolve gas concentrations in Fe-zeolite monolithic catalyst for various SCR reactions. They determined the catalyst length required to achieve desired NO_x conversions for various SCR reactions at different temperatures. Under the investigated conditions (Fe-beta zeolite catalyst, 1.2% Fe content, silica-alumina ratio 35:1, gas hourly space velocity (GHSV) = $28,000 \text{ h}^{-1}$, cell density: 400 cpsi), they found that the catalyst lengths needed to achieve 80% NO_x conversion at $300^\circ C$ were 2.4, 1.2 and 0.5 cm for the standard SCR, NO_2 -SCR and fast SCR reactions, respectively. These results confirm findings from other investigators [6,13] that an equimolar mixture of NO and NO_2 gives the highest NO_x conversion rates.

An important side reaction is the oxidation of NH_3 by O_2 . This reaction is undesirable since NH_3 is the reductant of NO_x . Both Fe- and Cu-zeolites catalyze NH_3 oxidation to N_2 :



Ammonia oxidation has been well studied on various zeolite catalysts in the literature [17,18]; both Fe- and Cu-zeolite catalysts have been found to be highly selective in oxidizing NH_3 to N_2 . For Fe-zeolite catalysts, NH_3 oxidation starts at higher temperature ($300^\circ C$) and is slower compared to that on Cu-zeolite (ca. $250^\circ C$). The consumption of NH_3 on Cu-zeolites is significant and leads to a sharp decrease in NO_x conversion activity at high temperatures [6,7]. In contrast, NH_3 oxidation is less pronounced on Fe-based zeolites, becoming important only at very high temperatures. Other side reactions like NO oxidation, ammonium nitrate formation and its decomposition to N_2O also take place on these catalysts [19].

Given the differences in activities of the Cu- and Fe-based catalysts, it seems plausible that a combination of Fe-zeolite and Cu-zeolite catalysts might achieve high NO_x conversions over a broader temperature range than the individual catalysts. A few literature studies considered such combined Fe- and Cu-zeolite systems [20,21]. Krocher and Elsener [20] studied various combinations of Fe-zeolite, Cu-zeolite and $V_2O_5/WO_3\text{--}TiO_2$ and found that a Fe-zeolite section followed by a Cu-zeolite (in series) gives higher NO_x conversion efficiencies. Girard et al. [21] carried out similar studies on combinations of Fe- and Cu-zeolite monolith catalysts and came to the same conclusion. In their study, they found that the series combinations of (33%) Fe-zeolite followed by (67%) Cu-zeolite gives the highest NO_x reduction efficiency throughout the temperature range. Similar studies of a series arrangement of Fe- and Cu-zeolite catalysts with different individual catalyst lengths were carried out by Theis and McCabe [22]. In an actual diesel engine exhaust aftertreatment system, a SCR unit is preceded by a diesel oxidation catalyst (DOC) unit, which has the function of oxidizing hydrocarbons to CO_2 and H_2O and NO to NO_2 . The NO oxidation generates the NO_2 needed to increase the effectiveness of the downstream SCR. However, the high cost of Pt is a major issue for the DOC unit. It is therefore of practical interest to develop alternative, more cost-effective SCR catalysts that can achieve high NO_x removal efficiencies with a reduced reliance on NO_2 generation using expensive precious metals (e.g. Pt).

The approach of combining two or more distinct catalysts to achieve improved performance has been considered in other reaction systems [23–25]. Xu et al. [24] used a physical mixture of zeolites with Na-rich, Fe-Cu Fischer-Tropsch catalysts to get improved activity for the hydrogenation of carbon dioxide. A few other studies [25–28] reported the use of so-called dual-layer monolithic catalysts for SCR of NO_x with hydrocarbons (e.g. propene) as reducing agents. The particular catalyst had a Pt/Al_2O_3 or Pt/SiO_2 in the bottom layer and, H- or Cu-zeolite (ferrierite or ZSM-5) in the top layer. The idea is to use the precious metal (e.g. Pt/Pd) in the bottom layer to oxidize NO to NO_2 which then diffuses back to be reduced by hydrocarbons (e.g. propene) in the upper layer containing a zeolite. The dual layer catalysts were found to be superior for NO_x reduction compared to the single layer catalyst (e.g. Pt/SiO_2). To our knowledge no literature study has focused on such dual layer catalyst configurations using NH_3 as a reductant.

The objective of the current study is to determine if a dual-layer Fe/Cu zeolite catalyst can exhibit improved performance for lean NO_x reduction. To this end, we examine in detail various combinations of sequential brick and dual-layer catalysts. Our approach is to systematically vary the lengths of the Fe- and Cu-zeolite monoliths in order to identify superior axial configurations, along the lines of the aforementioned pioneering studies at Ford. Various catalysts

Table 1

Following catalysts were used to study the standard and fast SCR reaction.

Catalyst	Catalyst description	Cu-zeolite loading (wt.%)	Fe-zeolite loading (wt.%)
Catalyst-A	Commercial Cu-zeolite (provided by BASF)	23	0
Catalyst-B	Commercial Fe-zeolite (unnamed supplier)	0	24
Catalyst-C	CuZ-12 on Catalyst B	12	24
Catalyst-D	FeZ-12 on Catalyst A	23	12
Catalyst-E	CuZ-25	25	0
Catalyst-F	FeZ-24	0	24
Catalyst-G	Combined FeCuZ-24 catalyst	12	12
Catalyst-H	CuZ-13 on FeZ-12	13	12
Catalyst-I	FeZ-16 on CuZ-8	8	16
Catalyst-J	FeZ-12 on CuZ-12	12	12
Catalyst-K	FeZ-8 on CuZ-16	16	8
Catalyst-L	FeZ-15 on CuZ-15	15	15
Catalyst-M	FeZ-10 on CuZ-20	20	10

are then tested in terms of NO_x removal efficiencies during the standard SCR reaction. Several dual layer catalysts having different washcoat loadings of Fe- and Cu-zeolite catalysts are compared for the standard and fast SCR reactions. The findings are interpreted in terms of the current understanding of lean NO_x reduction on zeolite-based catalysts.

2. Experimental

2.1. Catalyst preparation: ion exchange

We used both commercial and in-house synthesized Cu- and Fe-zeolite monolithic catalysts. The commercial Cu-zeolite catalyst was supplied by BASF (Iselin, NJ). It is a small-pore Cu-chabazite type catalyst, established in patents and communicated in recent papers to possess excellent activity and hydrothermal stability [29–31]. More detail about the synthesis and structure of this Cu-chabazite catalyst can be found in [31]. The Cu loading was about 2.5%. The commercial washcoated Fe-zeolite (ZSM-5 type) catalyst was supplied by an unnamed catalyst manufacturer. The sample had a Fe loading of about 3 wt.% in the monolith washcoat. Both the commercial samples had a cell density of 400 cpsi and effective washcoat thickness of about 45–50 μm . Additional washcoated monolith catalysts were synthesized in-house using catalyst powders. Fe-zeolite (ZSM-5) powder with Fe-content of about 3% (by wt.) was provided by Sud-Chemie (Munich, Germany) while the Cu-zeolite (ZSM-5) powder was synthesized by a conventional ion-exchange process briefly described below. Cordierite monolith cores (400 cpsi) were used as the support.

For the in-house synthesized Cu-ZSM-5 catalysts, the NH_4^+ form of zeolite (NH_4 -ZSM-5, Sud-Chemie Munich, Germany) powder with a Si/Al ratio of 25 was used as the starting material. The NH_4 -ZSM-5 powder was calcined in a box furnace at 500 °C for 5 h to convert it to H-ZSM-5. The H-ZSM-5 powder was then ion-exchanged with 0.1 M NaNO_3 solution by continuously stirring for several hours. The Na-ZSM-5 powder, thus obtained, was filtered and dried. The ion-exchange with the Na^+ solution was repeated twice. The Na-ZSM-5 powder was then ion-exchanged with 0.02 M copper acetate solution. This step was carried out by continuous stirring of the solution for 24 h followed by filtration and drying. This step was repeated twice to get the final Cu-ZSM-5 powder which was then calcined for 5 h at 500 °C [7]. The Cu content of the in-house synthesized Cu-ZSM-5 powder was found to be about 2% (by wt.) with inductive coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. The basic zeolite type (ZSM-5) was the same for all the above Fe- and Cu-zeolite catalysts (except Cu-chabazite) used in this study and these catalysts have a BET surface area of about 350 m^2/g .

2.2. Catalyst preparation: monolith washcoating

Catalysts prepared and evaluated in this study are summarized in Table 1. We used a dip-coating method to deposit catalyst on the monolith pieces. Blank cordierite monolith samples with cell density of 400 cpsi and dimensions of 1 inch diameter by 3 inch length were supplied by BASF. In Table 1, the CuZ-XX and FeZ-XX nomenclatures are used to define catalyst properties. “-XX” denotes the weight% of zeolite loading on the blank monolith support after drying. The monolith washcoating technique was the same as described in our earlier study [11]. A catalyst slurry consisting of a mixture of zeolite powder, γ -alumina and water was prepared in the proportions 32 wt.% zeolite, 8 wt.% alumina, with the remainder water with a small amount of 0.1 N acetic acid added to obtain a pH of 3.5. Alumina served as the binder. The catalyst slurry was ball milled for 20 h to obtain a particle size in the range of 1–5 μm , a necessary step to obtain a more uniform washcoat. Multiple dip coating steps were needed to achieve a prescribed loading (based on weight%). After each dipping, air was blown through the monolith channels to remove excess slurry, and then the washcoated monolith piece was dried at around 120 °C for 1 h. Subsequent weight measurement tracks the catalyst loading. After the desired catalyst coating/loading was achieved, the washcoated monolith sample was calcined at 500 °C for 5 h.

Dual-layer catalysts were prepared as follows. The same Cu-ZSM-5 and Fe-ZSM-5 slurries were used to synthesize all the CuZ-XX and FeZ-XX catalysts (Table 1). To obtain the Cu-ZSM-5 layer on the commercial Fe-zeolite catalyst (Catalyst B), a Cu-ZSM-5 slurry was deposited using the dip-coating technique. This resulted in Catalyst C comprising a CuZ-12 layer on the commercial Fe-zeolite. Similarly, in order to deposit a Fe-ZSM-5 layer on the commercial Cu-zeolite (catalyst A), Fe-ZSM-5 slurry was deposited the prescribed number of times and the same 12 wt.% loading of the top layer was achieved; this was Catalyst D. Catalysts E and F were obtained by repeating the dip coating till the desired 24–25 wt.% loading was achieved. For catalyst H, the FeZ-12 layer was first deposited on a blank monolith support followed by the deposition of the CuZ-13 layer. For the rest of the dual layer catalysts (I–M), a CuZ-XX layer was first deposited on the blank monolith support followed by the deposition of a FeZ-XX layer. In order to avoid the possible leaching of metal from the underlying layer during the coating of a second layer, we dried and calcined the catalyst coated with the first layer at 500 °C. Only then was the second layer was deposited. Finally, the washcoated catalysts were subjected to calcination at a slow temperature ramp of ca. 23 °C/h up to and maintained at 500 °C for 5 h. This deliberate calcination reduced the likelihood of crack formation in the washcoat layer.

The hydrothermal stability of the dual-layer catalysts (L and M) was evaluated. The catalysts were subjected to two different

temperatures of 600 °C and 700 °C for 6 h in the presence of 5% feed water and Ar as a balance gas. These are typical catalyst degreening (or aging, if for very long time) conditions. The standard SCR experiments were then repeated on catalysts L and M and results were compared to those obtained before the catalyst aging/degreening.

In order to investigate the issue of possible migration and hence mixing of the Fe and Cu metals from one layer to another at higher temperatures, we carried out energy dispersive spectroscopy (EDS) (JEOL JSM-6330F) analysis of both the fresh and the degreened (or aged) samples. For this purpose, we selected six different points along the corner of the washcoated monolithic catalyst channel where the washcoat was thicker and two different points near the center of the channel where the washcoat was thinner. At these points we investigated the presence of various metal elements using EDS analysis. The EDS results are shown later.

2.3. Bench-scale reactor set-up

The experimental setup included a gas supply system, a reactor system, an analytical system and a data acquisition system. Details of the apparatus are described elsewhere [32]. A monolith catalyst wrapped with a ceramic fiber was placed inside a quartz tube reactor mounted in a tube furnace. The quartz tubes used for this study were 40.6 cm long with an internal diameter of 0.81 cm and an outer diameter of 1.27 cm. In most of the experiments, we used 2 cm length and 34 channels of the monolith piece. This corresponds to a gas hourly space velocity (GHSV) (represented as the ratio volumetric flow rate calculated at standard temperature and pressure to the monolith brick volume) of 57,000 h⁻¹. The typical gas linear velocity during the experiments was calculated as a function of temperature and was found to be in the range of 0.6–1.2 m/s. The furnace temperature was adjusted with a temperature controller. A FT-IR spectrometer (Thermo-Nicolet, Nexus 470) was positioned downstream of the reactor to analyze various effluent gases including NH₃, NO, NO₂, N₂O and H₂O. A quadrupole mass spectrometer (QMS; MKS Spectra Products; Cirrus LM99) was used to measure N₂.

2.4. Steady-state reactor experiments

Several steady-state experiments were carried out on the catalysts described in Table 1. The experiments included NH₃ oxidation, standard SCR and fast SCR reactions. The space velocity was fixed at the same 57,000 h⁻¹ unless otherwise noted; Argon (Ar) was used as a balance gas and the total flow rate was maintained constant at 1000 sccm. Prior to reaction, each catalyst was exposed to 5% O₂ in Ar at 500 °C temperature for 30 min. The catalyst temperature was then reduced down to ambient temperature before each experiment was started. All the experiments were carried out in the temperature range of 150–550 °C and sufficient time was given to reach the steady state effluent concentrations.

The NH₃ oxidation reaction was studied on catalysts A and B of different lengths. The feed consisted of 500 ppm NH₃, 5% O₂ and 2% water. The standard SCR reaction was studied on all the catalyst samples listed in Table 1. For catalysts A and B, different lengths in the range of 4 mm to 2 cm were used to examine the effect of contact time. The space velocity was 114,000 h⁻¹ for the shorter catalyst piece (1 cm) and 57,000 h⁻¹ for the longer catalyst piece (2 cm). This helped in obtaining conversion data as a function of catalyst length. The standard SCR feed consisted of 500 ppm NO, 500 ppm NH₃, 5% O₂ and 2% water for all the experiments.

The effect of feed NO₂ was studied on catalysts A, F and K by using a feed consisting of an equimolar mixture of NO and NO₂ (250 ppm each), 500 ppm NH₃, 5% O₂ and 2% water in the temperature range of 180–550 °C. Finally, we used Fe-zeolite catalysts of different washcoat loadings, different washcoat thicknesses and

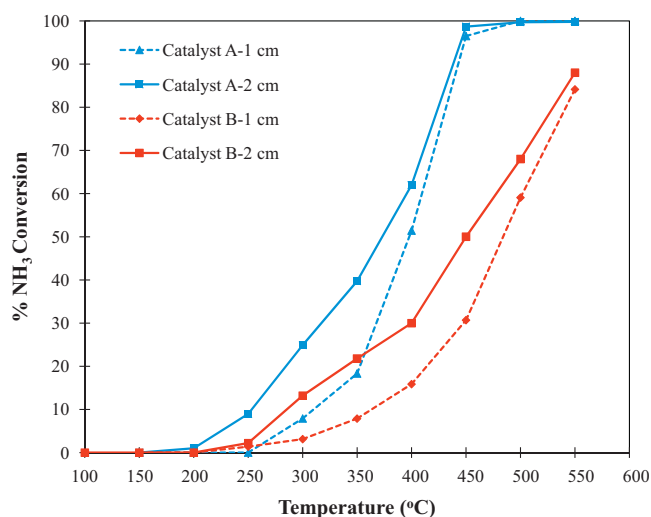


Fig. 1. Steady state NH₃ conversions obtained during the NH₃ oxidation reaction studied on commercial Cu-(catalyst A) and Fe-zeolite (catalyst B) catalysts with two different lengths of 1 and 2 cm.

Total flow rate = 1000 sccm, balance gas: Ar. Space velocity: 57,000 h⁻¹ (2 cm) and 114,000 h⁻¹ (1 cm).

Feed: 500 ppm NH₃, 5% O₂, 2% water. Temperatures studied: 150–550 °C.

lengths to study the existence and extent of mass transfer limitations during the standard and fast SCR reactions.

3. Results and discussion

Before presenting the data for the dual layer catalysts, representative results are reported for the single-layer commercial catalyst to establish conversion trends with temperature and space velocity. These data were also useful for justifying and interpreting the subsequent sequential Fe/Cu monolith configurations.

3.1. Ammonia oxidation: catalyst type and length effects

NH₃ oxidation reaction was carried out on both the Fe- and Cu-zeolite commercial catalysts using two different catalyst lengths (1 and 2 cm). These experiments identified the conditions (temperature, space velocity) needed to achieve a prescribed conversion. Fig. 1 clearly shows that the commercial Cu-zeolite (Cu-Z) is more active than the commercial Fe-zeolite (Fe-Z). While the metal loadings are not the same and the zeolites are different types, the trends are nevertheless consistent with those reported in previous studies [6,7,11]. On the 2 cm long Cu-Z (Fe-Z) catalyst the reaction commenced at about 200 °C (250 °C). Nearly complete NH₃ conversion was achieved at about 450 °C for Cu-Z (catalyst A), while only 88% conversion was achieved on Fe-Z (catalyst B) at 550 °C. On Cu-Z, a length of 2 cm provided sufficient contact time to achieve nearly complete NH₃ conversion by 400 °C. The results show that for temperatures exceeding 400 °C up to half of the catalyst (A) was unused.

The results for the commercial Fe-zeolite catalyst (B) using pieces of two different lengths (1 and 2 cm) exhibited somewhat different behavior (Fig. 1). Unlike Cu-Z, the conversion never reached 100% for temperatures up to 550 °C. A noted difference in conversion was observed for the catalysts of 1 and 2 cm length for temperatures below 550 °C. At 550 °C, there was a slight difference in conversions obtained on the two catalysts with different lengths.

3.2. Standard SCR reaction: catalyst type and length effects

The standard SCR reaction (reaction (1)) utilized NO, NH₃ and O₂ in the feed stream. All of the catalysts listed in Table 1 were used

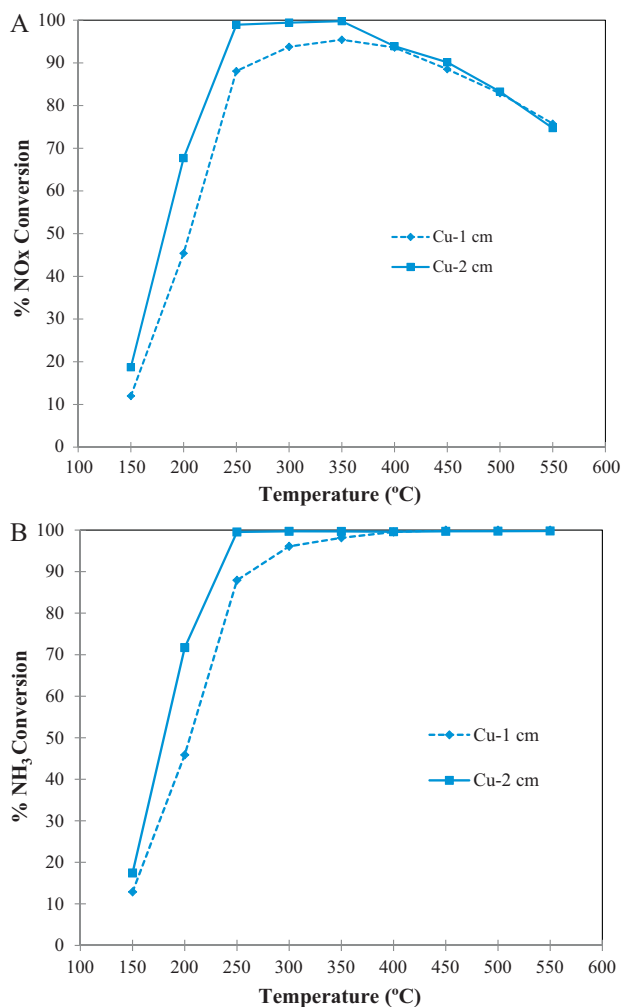


Fig. 2. Steady state (A) NO_x and (B) NH₃ conversions obtained during the standard SCR reaction studied on commercial Cu-zeolite catalyst (A) with two different lengths of 1 and 2 cm.

Total flow rate = 1000 sccm, balance gas: Ar. Space velocity: 57,000 h⁻¹ (2 cm) and 114,000 h⁻¹ (1 cm). Feed: 500 ppm NO, 500 ppm NH₃, 5% O₂, 2% water. Temperatures studied: 150–550 °C.

in this part of the study. First we compared the effect of monolith length on the NO_x conversion for the commercial Cu- and Fe-zeolite catalysts (A and B). The steady state NO_x conversions obtained on Cu-zeolite catalysts with two different lengths of 1 and 2 cm are compared in Fig. 2A. The Cu-zeolite data show that very high NO_x reduction activity is achieved at low temperature. For example, the NO_x conversion approached 68% for the 2 cm long catalyst at 200 °C and was essentially 100% in the temperature range of 250–350 °C. Beyond this range the NO_x conversion decreased. This decrease is attributed to the oxidation of the reductant NH₃, which achieves a high conversion at these conditions as shown in earlier experiments (Fig. 1). Fig. 2B shows there is an absence of NH₃ in the effluent for the 2 cm Cu-Z catalyst (A) (100% conversion at T ≥ 250 °C) and confirms the complete consumption of feed NH₃ by the NH₃ oxidation side reaction. The same standard SCR experiments on the shorter, 1 cm long Cu-zeolite catalyst resulted in lower NO_x conversions for temperatures below 250 °C. However, for temperatures beyond the conversion maximum, there was little effect of the catalyst length. This clearly indicates that a 1 cm catalyst provides sufficient residence time to obtain the high NO_x conversion at that temperature and that a large fraction of the 2 cm catalyst was not needed. The depletion of NH₃ (by oxidation) is undoubtedly responsible for the

near coincidence in the conversions for the two catalysts beyond the conversion maxima.

The consumption of NH₃ by oxidation increases the reactor length needed to achieve complete NO_x conversion. Balakotaiah and West [33] derived various correlations to estimate the limiting reactant conversion in various catalytic monoliths of arbitrary shapes and found that the conversion depends mainly on the transverse Peclet number (*P*) when the flow is fully developed and the reaction is fast. An estimate of the *P* enables one to determine the upper bound of the conversion for a single irreversible reaction operated in the mass transfer controlled regime. That is, the upper bound value approaches 99% as *P* decreases. *P* is defined as

$$P = \frac{R_{\Omega 1}^2 \langle u \rangle}{LD_f} \quad (5)$$

where *R*_{Ω1} is the effective transverse diffusion length, *u* is the average velocity inside monolith channel, *L* is the length of the monolith channel and *D_f* is the diffusivity of a species in the fluid phase. A typical value of *P* is about 0.06 for most of our experiments using monolithic catalyst of 2 cm length. The value of *P* increases with decreasing catalyst length or increasing space velocity. According to the correlations provided by Balakotaiah and West [33], nearly complete reactant conversion can be achieved even with a *P* value of 0.4. Using these correlations, we estimated that 2 mm of catalyst length (for a monolith with 34 channels) would be sufficient to approach complete NO_x conversion on both the Cu- and Fe-zeolite catalysts as the reaction is very fast at these temperatures (at T ≥ 450 °C). This further confirms that the presence of the NH₃ oxidation side reaction reduces the NO_x conversion (i.e. NH₃ is depleted) on both the catalysts.

The performance of the commercial Fe-zeolite catalyst was examined by measuring the NO_x conversion during the SCR reaction for several different lengths (Fig. 3A). Unlike the commercial Cu-zeolite, the activity of the Fe-zeolite was quite low for temperatures below 350 °C. There was also a substantial difference in the NO_x conversion on catalysts with different lengths between 0.4 and 2 cm. At higher temperatures (≥ 400 °C), the NO_x conversions reached an asymptotic value of ~93% for the catalysts with lengths 1 cm and above. The data indicate that a 1 cm long Fe-zeolite catalyst would provide sufficient catalyst amount and contact time required to achieve the desired NO_x conversion at higher temperatures (>350 °C) as the entire 2 cm length was not utilized. The NO_x conversions never reached 100% because of the NH₃ oxidation side reaction which consumed the reductant NH₃. Fig. 3B shows the steady state NH₃ conversions obtained during the above standard SCR experiments studied on Fe-zeolite catalysts of different lengths. In Fig. 4, we represent the NO_x conversion as a function of the space velocity for several catalyst temperatures. These results show that the NO conversion decreases with increasing space velocity and comparable NO_x reduction activities were achieved for space velocities below 110,000 h⁻¹ at higher temperatures.

3.3. Fe- and Cu-zeolite series monolith catalyst

The data presented thus far show that the commercial Cu-zeolite catalyst is an effective NO_x reduction catalyst at lower temperatures (≤ 350 °C) while the commercial Fe-zeolite is superior at higher temperatures (≥ 400 °C), in agreement with the literature studies [6,10]. A Cu-zeolite catalyst of 1 cm length is sufficient to achieve a NO_x conversion exceeding 90% at lower temperatures (250–350 °C). For the commercial Fe-zeolite catalyst, 1 cm length is sufficient to achieve 90% conversion in the higher temperature range (400–550) °C. These conversion versus volume performance data are utilized in the next set of experiments in which we examine series combinations of the two catalysts.

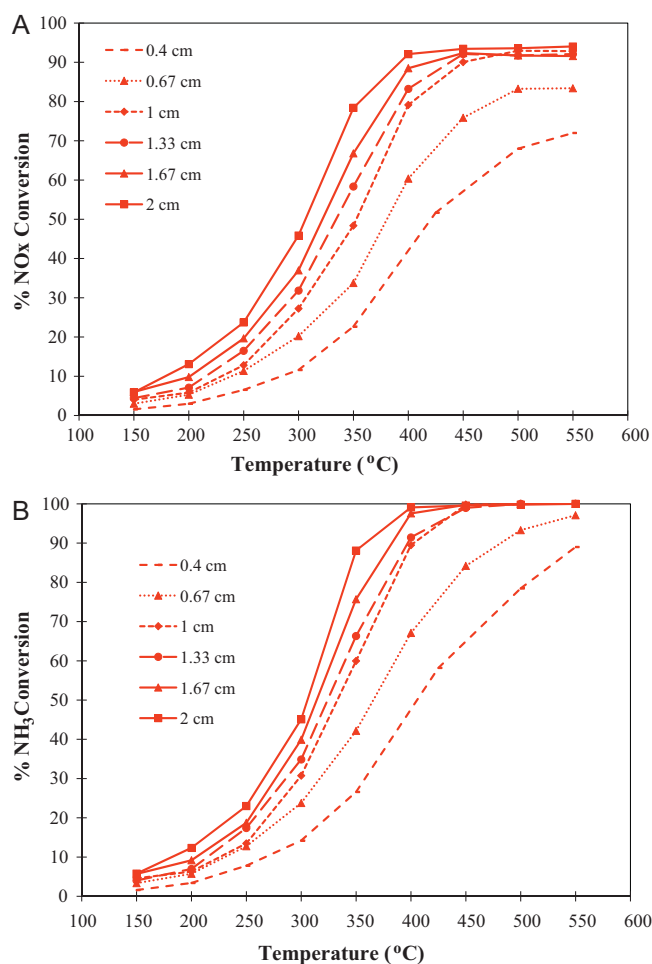


Fig. 3. Steady state (A) NO_x and (B) NH₃ conversions obtained during the standard SCR reaction studied on the commercial Fe-zeolite catalyst (B) with different lengths in the range of 0.4–2 cm. Total flow rate = 1000 sccm, balance gas: Ar. Feed: 500 ppm NO, 500 ppm NH₃, 5% O₂, 2% water. Temperatures studied: 150–550 °C.

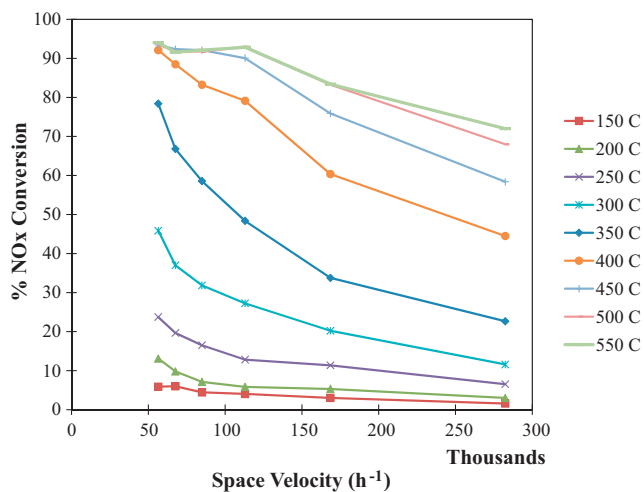


Fig. 4. Steady state NO_x conversions obtained during the standard SCR reaction studied on the commercial Fe-zeolite catalyst (catalyst B) as a function of space velocity (h⁻¹).

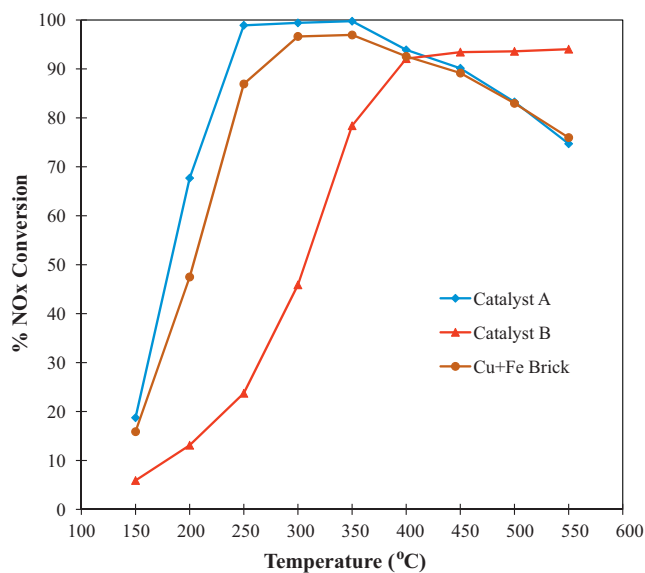


Fig. 5. Steady state NO_x conversions obtained during the standard SCR reaction studied on catalyst A, catalyst B and combined system of series arrangement of catalyst A (1 cm Cu brick in front) followed by catalyst B (1 cm Fe brick). Total length of the monolithic reactor: 2 cm. Total flow rate = 1000 sccm, space velocity = 57,000 h⁻¹, balance gas: Ar. Feed: 500 ppm NO, 500 ppm NH₃, 5% O₂, 2% water. Temperatures studied: 150–550 °C.

The first series monolith configuration considered was a Cu-zeolite followed by a Fe-zeolite. Specifically, a 1 cm long piece of the commercial Cu-zeolite (Catalyst A) was followed by a 1 cm long piece of commercial Fe-zeolite (B). The experimental conditions used previously for the individual catalysts were repeated here for the sequential configuration. The results provided in Fig. 5 compare the 2 cm total length, Cu (1 cm)/Fe (1 cm) monolith series combination with the 2 cm long individual Cu-zeolite (A) and Fe-zeolite (B) samples. The sequential configuration exhibited behavior very similar to that of the Cu-Z (A) catalyst: a sharply increasing NO_x conversion at low temperature (<300 °C), a maximum NO_x conversion exceeding 95% at intermediate temperature (300–350 °C) and a decreasing conversion at high temperature (>400 °C). These data clearly indicate that, at low temperature, most of the NO_x reduction occurs in the Cu-Z (A) section and that the Fe-Z (B) catalyst is not utilized. At higher temperature there is nearly complete overlap of the conversions obtained for the Cu-Z/Fe-Z monolith and the Cu-Z (A) monolith. This suggests that the high rate of NH₃ oxidation on the Cu-zeolite prevents utilization of the Fe-zeolite section for NO_x reduction. Thus, in effect, the Fe-zeolite section is not utilized over the entire temperature range. Therefore, a series catalyst configuration in which Cu-zeolite is followed by the Fe-zeolite does not improve the NO_x reduction performance at high temperatures. For this reason we did not consider any other Cu-Z/Fe-Z combinations in subsequent experiments.

The results are more encouraging when the catalyst arrangement is reversed and the Fe-zeolite catalyst is positioned in front of the Cu-zeolite. Here we studied three different combinations for this Fe-Z/Cu-Z series arrangement. The total catalyst length was fixed at 2 cm while varying the individual lengths of Fe- and Cu-zeolite sections; specifically:

- Series 1: Fe (1.33 cm/67% of total length) + Cu (0.67 cm/33%).
- Series 2: Fe (1 cm/50%) + Cu (1 cm/50%).
- Series 3: Fe (0.67 cm/33%) + Cu (1.33 cm/67%).

Results obtained with these three series arrangements are shown in Fig. 6. For comparison, the 2 cm long Cu-zeolite

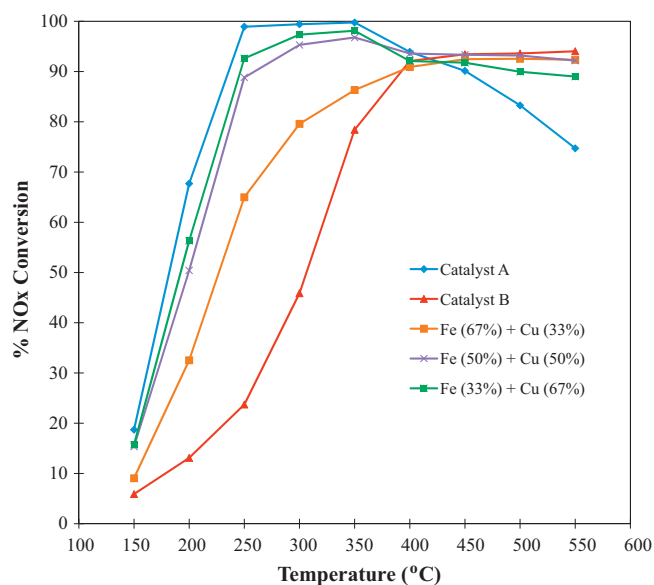


Fig. 6. Steady state NO_x conversions obtained during the standard SCR reaction studied on various catalysts: catalyst A, catalyst B, and combined system of series arrangement of catalyst B (in front) (1.33 cm, 1 cm and 0.67 cm bricks) followed by catalyst A (0.67 cm, 1 cm and 1.33 cm bricks). Total length of the monolithic reactor: 2 cm.

Total flow rate = 1000 sccm, space velocity = $57,000 \text{ h}^{-1}$, balance gas: Ar. Feed: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , 2% water. Temperatures studied: 150–550 °C.

(catalyst A) and Fe-zeolite (catalyst B) monolith results are also provided. For Series 1, the NO_x conversions exceeded the Fe-Z only conversion at lower temperatures ($\leq 350^\circ\text{C}$) although the conversion was still considerably lower than the Cu-Z only catalyst (A). At higher temperatures ($\geq 400^\circ\text{C}$), the conversion obtained for Series 1 was nearly identical to the Fe-Z only sample (catalyst B). For Series 2, the NO_x conversion increased significantly at lower temperatures and remained close to that of the Fe-Z only catalyst at higher temperatures. For Series 3 these trends continued. The NO_x conversion at low temperature approached that of the Cu-Z only catalyst without much loss in conversion at high temperature.

These results show that the overall NO_x conversion can be maintained at a relatively high level over a wide temperature range by utilizing a Fe-Z/Cu-Z series configuration. The findings are in agreement with earlier results of Girard et al. [21] and suggest that there exists an optimal Fe-Z/Cu-Z configuration in terms of NO_x conversion for the standard SCR reaction. By positioning Fe-Z in front of Cu-Z, the high NO_x reduction activity of Fe-Z is exploited at high temperature while avoiding the detrimental NH_3 oxidation activity of Cu-Z. At low temperature the low activity of Fe-Z shifts the bulk of the NO_x reduction downstream to the Cu-Z section.

3.4. Mixed Fe- and Cu-ZSM-5 layer monolith catalyst

The series configuration results provide the incentive to explore a combination of the Fe- and Cu-zeolite catalysts in a layered structure. In our recent work, we have found that washcoat diffusion can limit the overall rate during standard-, fast- and NO_2 -SCR [34]. Specifically, we have shown improved performance (conversion) when a fixed amount of Fe- or Cu-zeolite is spread over a longer monolith. In this section, we present results obtained on various in-house synthesized dual layer monolithic SCR catalysts.

In order to conduct a meaningful comparison, our approach is to synthesize monolith catalysts having a fixed total washcoat loading (mass basis) and monolith length while varying the mass fractions of the Cu-ZSM-5 and Fe-ZSM-5. Then the conversion of NO_x for each

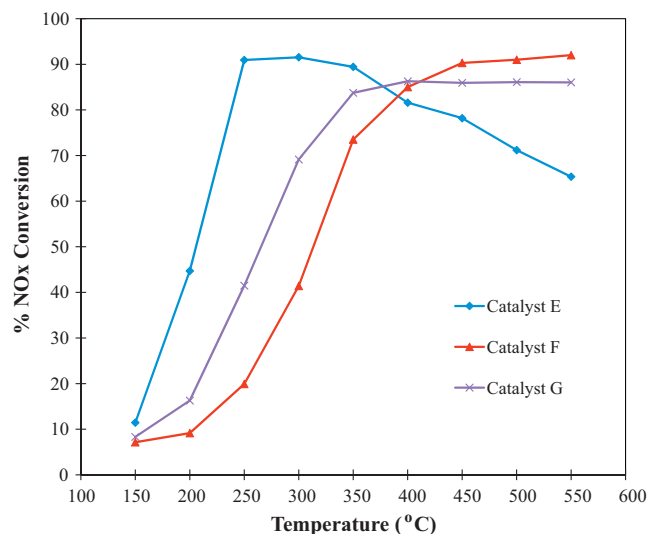


Fig. 7. Steady state NO_x conversions obtained during the standard SCR reaction studied on various in-house synthesized catalysts E, F and G. Total length of the monolithic reactor: 2 cm. Total flow rate = 1000 sccm, space velocity = $57,000 \text{ h}^{-1}$, balance gas: Ar.

Feed: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , 2% water. Temperatures studied: 150–550 °C.

dual-layer catalyst is compared to the conversions obtained for the single layer Cu-ZSM-5 and Fe-ZSM-5 catalysts. The total washcoat loading was selected to be 24–25 wt.%. The metal loading for the Cu and Fe were fixed by using the same exchanged zeolite samples. All other experimental conditions were kept the same as described earlier.

First we show the results obtained for single-layer catalysts CuZ-25 (catalyst E) and FeZ-24 (catalyst F), each of total length 2 cm. Fig. 7 shows the NO_x conversions obtained during the standard SCR reaction carried out on these catalysts. The NO_x conversion trends obtained for catalysts E and F are comparable to the results obtained with the commercial catalysts A and B, respectively (Figs. 2 and 3). The only difference is a slightly lower activity for the in-house synthesized catalysts. Also shown in Fig. 7 is the NO_x conversion for a mixed washcoat catalyst (G) for which the loading of Cu-ZSM-5 and Fe-ZSM-5 were identical (12 wt.%). This catalyst was prepared by coating a blank monolith with a slurry containing a physical mixture of the two metal exchanged zeolites.

The mixed washcoat catalyst G gave a NO_x conversion effectively bound above and below by the conversions obtained for catalysts E and F. Thus, the NO_x conversion activity obtained on this catalyst could be considered as an average of the conversions obtained on the two separate catalysts. In the lower temperature range ($T < 400^\circ\text{C}$), the conversion was bound above by the Cu-ZSM-5 and below by the Fe-ZSM-5. In the higher temperature range ($T > 400^\circ\text{C}$) the conversion was bound above by the Fe-ZSM-5 and below by the Cu-ZSM-5. The exception to the average result is noted at the intermediate temperature of 400°C , in which the layered catalyst NO_x conversion slightly exceeds the conversions of the single metal catalysts. Next we show that the physical mixture is not the best approach to combining the two metal-exchanged zeolites in a layered structure.

3.5. Dual layer Fe-ZSM-5/Cu-ZSM-5 monolith catalysts

A group of synthesized dual-layer catalysts were evaluated and compared to the performance of the single-layer Cu-ZSM-5 and Fe-ZSM-5 catalysts. The properties of catalysts H–M are provided in Table 1.

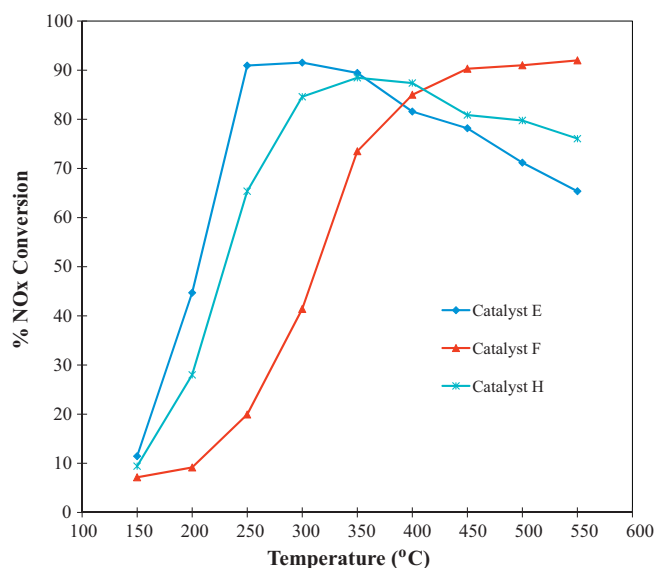


Fig. 8. Steady state NO_x conversions obtained during the standard SCR reaction studied on various in-house synthesized catalysts E, F and H. Total length of the monolithic reactor: 2 cm. Total flow rate = 1000 sccm, space velocity = $57,000 \text{ h}^{-1}$, balance gas: Ar. Feed: 500 ppm NO , 500 ppm NH_3 , 5% O_2 , 2% water. Temperatures studied: 150–550 °C.

As shown earlier, the series combination of Cu-zeolite section followed by Fe-zeolite section had similar performance compared to the Cu-only catalyst and did not show any improvement in the NO_x conversion at higher temperatures. We carried out an experiment of a monolith with Cu-ZSM-5 as the top layer and Fe-ZSM-5 as the bottom layer to see if comparable results would be obtained. The total loading was fixed at 25 wt.% with nearly equal loadings of the Cu and Fe layers. The trends obtained with this catalyst H shown in Fig. 8 are similar to those obtained for the Cu-Z/Fe-Z series configuration (Fig. 5). The NO_x conversion for catalyst H exceeded the conversion obtained for Fe-ZSM-5 (catalyst F) for temperatures up to 400 °C. But at higher temperatures (>400 °C), the NO_x conversion approached that of the Cu-ZSM-5 (catalyst E). In light of the Cu-Z/Fe-Z series results, these results were not surprising. With the dual-layer configuration, reactants diffuse into the washcoat, obviously encountering the top layer first. This is comparable but not equivalent to encountering the first section in a series of bricks configuration. Thus, at low temperature, the SCR reaction occurs in the more active Cu-ZSM-5 top layer while the underlying, less active Fe-ZSM-5 layer is essentially not utilized. Similarly, at high temperature, the active Cu-ZSM-5 is encountered first and catalyzes the reactions. But at higher temperatures the ammonia oxidation activity is significant, resulting in the consumption of ammonia in the top layer. This results in a lack of availability of NH_3 for the complete NO_x reduction at higher temperatures. That the drop in the NO_x reduction activity at high temperature was somewhat less compared to the Cu-only (catalyst E) catalyst suggests that some reacting species diffuse through the top Cu-ZSM-5 layer to react on the more selective, underlying Fe-ZSM-5 catalyst. The NO_x reduction occurs on catalysts present in both the layers. Thus, the dual-layer catalyst system with Cu-zeolite on top of Fe-zeolite exhibits improved performance (compared to Fe-only catalyst) at lower temperature but has the drawback of reduced NO_x conversions at higher temperatures. No other compositions of the Cu-ZSM-5 on Fe-ZSM-5 were examined for this reason.

We turned our attention to dual-layer catalysts with the Fe-zeolite layer on top of the Cu-zeolite layer. Again, we fixed the total washcoat loading to 24–25% in order to conduct a meaningful

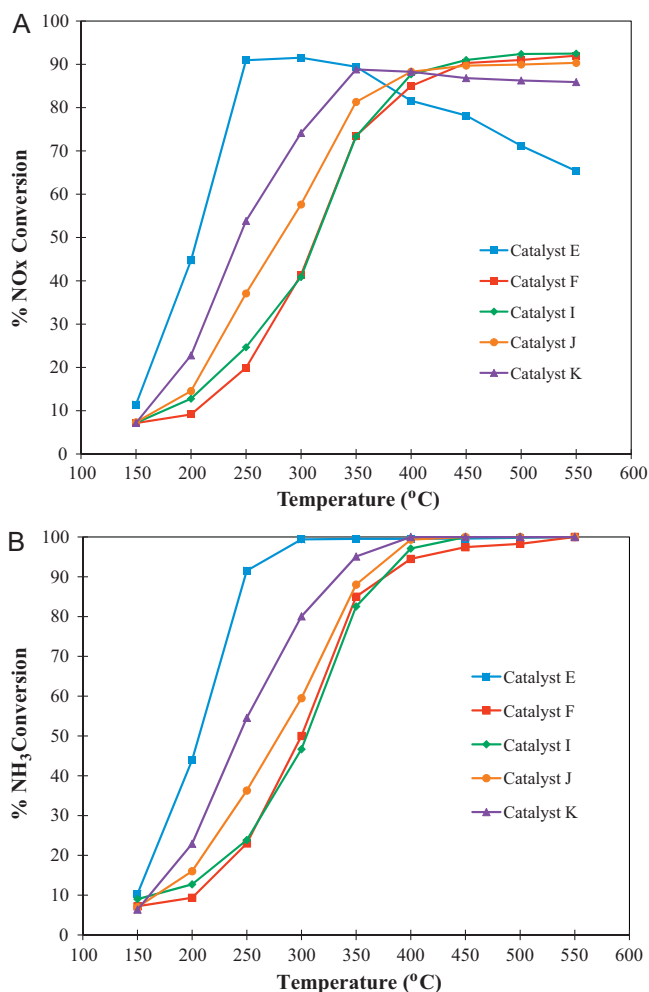


Fig. 9. Steady state (A) NO_x and (B) NH_3 conversions obtained during the standard SCR reaction studied on various in-house synthesized catalysts E, F, I, J and K. Total length of the monolithic reactor: 2 cm. Total flow rate = 1000 sccm, space velocity = $57,000 \text{ h}^{-1}$, balance gas: Ar. Feed: 500 ppm NO , 500 ppm NH_3 , 5% O_2 , 2% water. Temperatures studied: 150–550 °C.

comparison with the single-layer Cu-ZSM-5, Fe-ZSM-5 and mixed washcoat catalysts. Fig. 9A shows the standard SCR results for catalysts I–K in which the fraction of Fe-ZSM-5 was decreased from 16 to 8 wt.% while maintaining a fixed total loading of 24 wt.%. The operating conditions were the same in all of the experiments. The data show that as the fraction of Fe-ZSM-5 (Cu-ZSM-5) decreases (increases) there is a progressive increase in the low temperature conversion accompanied by a much less pronounced decrease in high temperature conversion. Specifically, catalyst I showed a slightly higher NO_x reduction activity than the Fe-only sample (catalyst F) for temperatures below 300 °C while at higher temperature (>350 °C) the NO_x reduction activity was nearly identical on both the catalysts. Following earlier discussion, the reason for this trend is that the thinner Cu-zeolite layer positioned underneath the thicker Fe-zeolite layer has only a small contribution to the overall conversion. That is, coupled reaction and diffusion in the top Fe-zeolite layer prevents the reacting species from penetrating the underlying Cu layer. The effect of a decrease in the Fe-zeolite top layer thickness and corresponding increase in the Cu-zeolite bottom layer thickness helps to confirm this trend. Fig. 9A shows an enhancement in the low temperature conversion for Catalysts J and K while the high temperature conversion is largely unaffected. For example, at 250 °C the NO_x conversion increases from 24 to 37 to

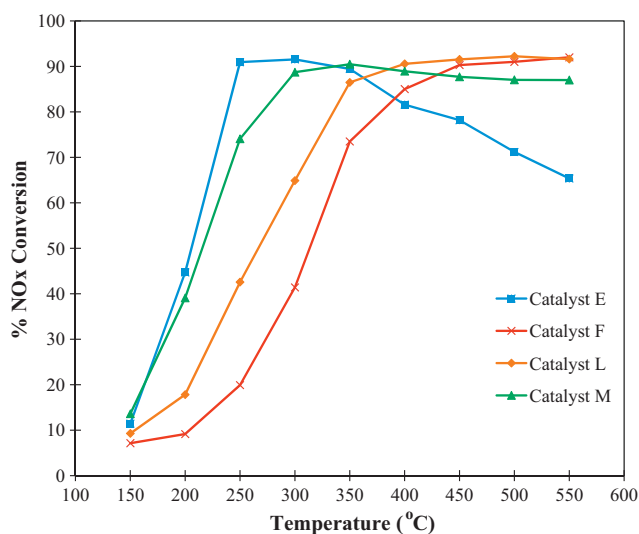


Fig. 10. Steady state NO_x conversions obtained during the standard SCR reaction studied on various in-house synthesized catalysts E, F, L and M. Total length of the monolithic reactor: 2 cm. Total flow rate = 1000 sccm, space velocity = $57,000 \text{ h}^{-1}$, balance gas: Ar. Feed: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , 2% water. Temperatures studied: 150–550 °C.

55% as the Fe-ZSM-5 loading is decreased from 16 to 12 to 8 wt.%, while at 500 °C the NO_x conversion varies from 92 to 90 to 87%. The increase at low temperature is clearly a result of the increase in the loading of the underlying Cu-ZSM-5 and decrease in the thickness of the relatively inactive Fe-ZSM-5 layer, which serves more as a non-catalytic diffusion barrier. The small conversion decrease at high temperature indicates some penetration of reacting species, in particular NH_3 , to the underlying Cu-ZSM-5 layer where it is oxidized. Again, the conversions obtained on all these catalysts never reached 100% because of the NH_3 oxidation side reaction. In Fig. 9B, we show the steady state NH_3 conversions obtained on catalysts E–K during the above mentioned standard SCR experiments. Fig. 9B clearly shows the complete consumption of NH_3 at higher temperatures on all the catalysts.

Comparing the three dual layered catalysts, catalyst K (1:2 Fe:Cu-zeolite ratio) clearly gives the highest NO_x reduction activity over the entire temperature range. The results indicate that for a fixed loading there exists an optimum Fe-ZSM-5 top layer thickness, similar to the aforementioned series configuration.

In order to pursue the NO_x enhancement with the dual-layer configuration further, we examined the effect of increasing the total washcoat loading while maintaining a smaller fraction of the Fe layer compared to the Cu layer. Fig. 10 shows the results for catalysts with a total washcoat loading of about 30% (by wt.). We intentionally focused on catalysts with mass fraction of Fe-ZSM-5 ≤ 0.5 . Fig. 10 shows the results for Catalysts L and M, which respectively correspond to Fe-Z(15)/Cu-Z(15) and Fe-Z(10)/Cu-Z(20). For comparison, the 24 wt.% single-layer Fe-ZSM-5 and Cu-ZSM-5 samples (catalysts E and F) are shown. The higher loading and thinner Fe-ZSM-5 top layer clearly shows further enhancement at low temperature while maintaining high conversion at high temperature. These results further underscore the existence of an optimal loading of Fe-zeolite (top layer) and Cu-zeolite (bottom layer).

3.6. Application to fast SCR

In the real exhaust aftertreatment system, the SCR unit is preceded by a DOC unit (containing a precious metal like Pt) which has the role of catalyzing the oxidation of hydrocarbons, CO and

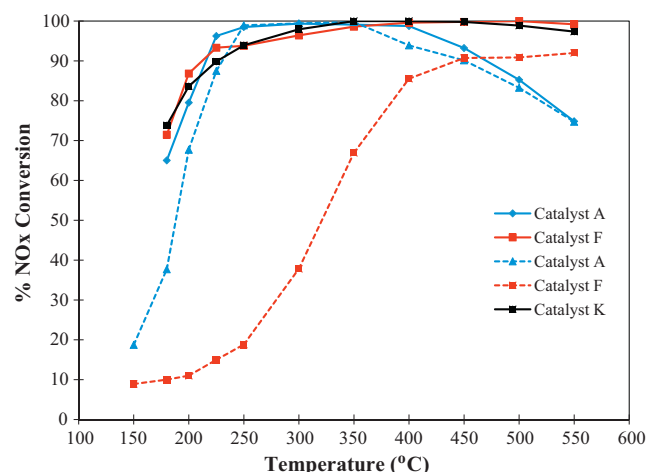


Fig. 11. Steady state NO_x conversions obtained during the fast SCR reaction studied on various catalysts. Total flow rate = 1000 sccm, space velocity = $57,000 \text{ h}^{-1}$, balance gas: Ar. Feed: 250 ppm NO, 250 ppm NO_2 , 500 ppm NH_3 , 5% O_2 , 2% water. Temperatures studied: 150–550 °C. Dashed lines show the NO_x conversions obtained during the standard SCR reaction.

NO. As previous literature studies have shown, the reduction of NO_x is enhanced significantly by NO_2 with the optimal feed ratio being $\text{NO}/\text{NO}_2 = 1$. The so-called “fast SCR” reaction system given by reaction (2) does not require the oxidation of NO to NO_2 in the SCR. It is now well accepted that the rate of SCR reaction increases in the presence of NO_2 (especially at lower temperatures) on both the Fe- and Cu-zeolite catalysts [13], although the rate increment is more dramatic for Fe-zeolite compared to Cu-zeolite catalyst. In the context of the current study, it is of interest to determine the potential for the dual layer catalyst when the feed contains NO_2 .

Here we show the results (Fig. 11) of NO_x conversion obtained during the fast SCR reaction on both the Fe- (catalyst F) and the commercial Cu-zeolite (catalyst A) and also on catalyst K as a representative case of the dual layer catalyst system (8 wt.% Fe-ZSM-5, 16 wt.% Cu-ZSM-5). A feed containing an equimolar mixture (250 ppm each) of NO and NO_2 was introduced in the presence of 500 ppm NH_3 , 5% O_2 and 2% water. As expected, the NO_x conversions increased dramatically for the Fe-zeolite (F) catalyst especially at lower temperatures compared to the case of standard SCR reaction. In addition, very high conversion of NO_x is obtained at higher temperatures (≥ 300 °C). In the presence of feed NO_2 , there is an enhancement in the NO_x reduction activity at lower temperatures even for the Cu-zeolite catalyst (A). But the effect was not as dramatic as that for the Fe-zeolite. The Cu-zeolite catalyst (A) exhibited similar trends in the NO_x conversion at higher temperatures for both the standard and fast SCR reactions. This includes the sharp decrease in the NO_x conversion at temperatures > 350 °C as a result of the consumption of the NH_3 reductant by oxidation.

The dual layer catalyst K exhibited remarkably high NO_x conversion ($> 90\%$) over the entire temperature range (250–550 °C). In fact, the NO_x reduction activity of this catalyst was comparable to the Fe-only system even at higher temperatures where it showed very stable NO_x reduction efficiency. These results demonstrate that the dual layer catalyst system with thinner Fe-zeolite layer on top of a thicker Cu-zeolite layer works well even for the case of fast SCR system which in some applications is more representative of an actual diesel exhaust system.

3.7. Coating commercial catalysts

The results shown so far establish that the dual-layer SCR catalyst system demonstrates superior performance during the

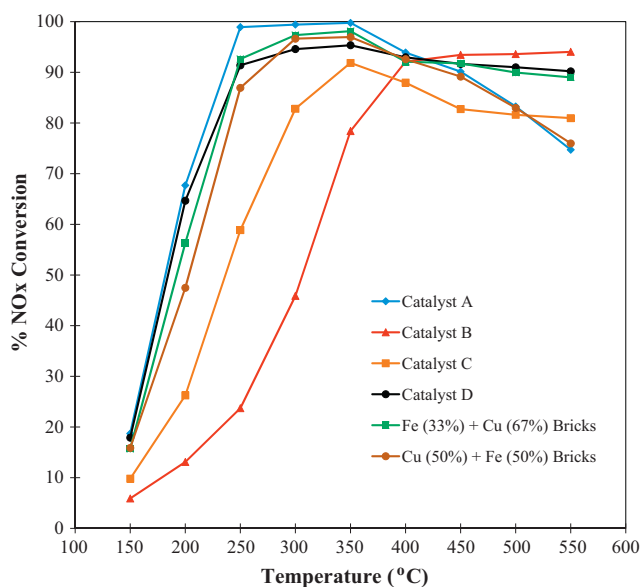


Fig. 12. Steady state NO_x conversions obtained during the standard SCR reaction studied on various catalysts A, B, C and D. Additional plots for the series arrangements of catalysts A and B are also shown. Total length of the monolithic reactor: 2 cm. Total flow rate = 1000 sccm, space velocity = $57,000 \text{ h}^{-1}$, balance gas: Ar. Feed: 500 ppm NO , 500 ppm NH_3 , 5% O_2 , 2% water. Temperatures studied: 150–550 °C.

standard and fast NO_x reduction over a wide temperature range. Figs. 9 and 10 results show that a Fe-Z/Cu-Z configuration can achieve over 90% conversion at temperatures up to 550 °C, a significant increase over the single component catalyst. As mentioned earlier, the results suggest that an optimal dual-layer catalyst composition exists that maximizes the NO_x conversion over a prescribed temperature range. A combination of additional experiments with modeling is needed to identify the optimal composition. The optimization study is ongoing in our group.

In order to examine the generality of the findings, we carried out an additional set of experiments in which the commercial Fe-zeolite and Cu-zeolite catalysts were coated with Cu-ZSM-5 and Fe-ZSM-5, respectively. Catalyst C was prepared by depositing a thin layer (12 wt.%) of Cu-ZSM-5 on the commercial Fe-zeolite (Catalyst B), while catalyst D was prepared by depositing a thin layer (12 wt.%) of Fe-ZSM-5 on the commercial Cu-zeolite (Catalyst A). The standard SCR reaction was studied on these catalysts under the same conditions as the previous experiments. Results obtained for Catalysts C and D are compared in Fig. 12 to the unmodified A and B samples, as well as to two of the monolith configurations. The comparison reveals excellent performance for Catalyst D. The NO_x conversion exceeds 90% over the 250–550 °C temperature range. Comparable performance is achieved for the sequential monolith configuration Fe-Z(33%)/Cu-Z(67%). These results with the commercial catalysts are in agreement with earlier results with the in-house synthesized dual-layer catalysts. The results also show that with the simple deposition of a thin layer of the Fe-exchanged zeolite the performance of a commercial Cu-zeolite can be improved significantly. The results obtained on the modified (dual layer) commercial catalysts were compared with the series arrangements of the catalyst bricks and the trends obtained with these two reactor systems were found to be similar.

3.8. Dual-layer metals distribution and thermal stability

A practical concern about the dual-layer catalyst performance is their durability at elevated temperatures. For example, were migration of the Fe and/or Cu to occur this might compromise the

Table 2

EDS analysis of the dual layer catalyst (catalyst L).

EDS analysis point	Fe peak	Cu peak	Fe (wt.%)	Cu (wt.%)
1	✓	×	2.37	0.30*
2	✓	×	3.81	0.01*
3	✓	×	3.28	0.1*
4	×	✓	0.51*	2.53
5	×	✓	0.05*	1.18
6	×	✓	0.16*	1.82

* Below detection limit of the instrument.

✓ Presence of peak for the particular element during EDS analysis.

× Absence of peak for the particular element during EDS analysis.

enhanced performance of the segregated metal-exchanged zeolite layers. To address this concern, Catalysts L and M were heated to 600 °C and 700 °C for 6 h in a 1000 sccm feed stream containing 5% water in Ar. The temperature was then brought down to the ambient temperature and the standard SCR reaction was carried out under the same conditions as before the thermal treatment. The NO_x reduction activity was found to be identical (within experimental error) to that of the previous case of fresh/unaged samples. Thus the catalyst was found to be stable and was able to sustain high temperatures of 700 °C without undergoing any physical/chemical changes. That said, prolonged aging that emulates sustained high load operation and/or filter regenerations may be necessary to assess whether migration eventually becomes an issue.

In order to study the distribution of Fe and Cu in the fresh and aged dual layer catalyst samples, we used energy dispersive X-ray spectroscopy (EDS) analysis. Fig. 13 depicts the shape of a typical washcoat in washcoated monolithic channel that we synthesized in-house by the dip-coating technique. As there was more catalyst deposition near the corner of a monolithic channel, we measured the local concentration at six distinct points separated by the same distance at one of the corners of the monolith (Fig. 13). The EDS “counts” provide a measure of the local concentration of Fe and Cu. The spatially resolved profile provides a semi-quantitative trend in the concentrations of the metal species. The data obtained at various points for degreened catalyst L is presented in Table 2. The top layer of the dual layer catalyst consisted of Fe-ZSM-5, within which we made EDS measurements at three points (labeled as 1–3 in Fig. 13). In this section of the washcoat we did not detect a clear peak for Cu while the Fe-peak was clearly visible. The bottom layer consisted of a Cu-zeolite layer. In this region no Fe peak was detected at the three labeled points 4–6 (Fig. 13) whereas Cu was detected. Thus the EDS analysis shows that the Fe- and Cu-zeolite layers remain intact even after degreening at high temperature and the two metals/layers do not migrate/mix. The reproducibility of SCR results obtained on catalysts even after the high temperature degreening confirm the stability of dual layer catalysts synthesized for this study.

3.9. Dual layer catalyst: working principle

The objective of using a dual layer SCR catalyst system was to achieve a distribution of Fe- and Cu-zeolite layers that maximizes the NO_x reduction activity over a wider temperature range than achievable with the individual metal-exchanged zeolites. Fig. 14 shows a schematic representation of the Fe- and Cu-zeolite dual layer catalyst concept. As discussed earlier, the Cu-based zeolite is an effective NO_x reduction catalyst at lower temperature whereas Fe-based zeolite is relatively inactive. At low temperature the Cu-zeolite layer is needed to achieve high NO_x reduction efficiency. A sufficiently thick Cu-zeolite coated with a thinner porous over-layer of Fe-zeolite should retain its NO_x reduction activity since the Fe-layer behaves essentially as an inactive diffusion barrier. In contrast, at higher temperatures, the ammonia oxidation reaction

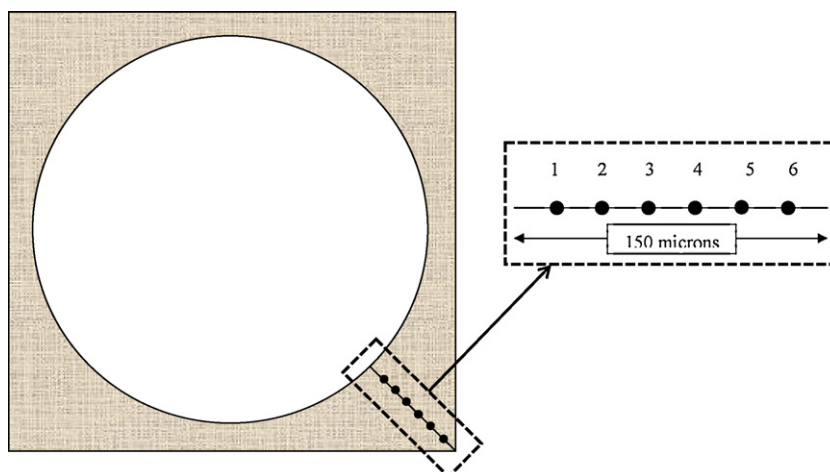
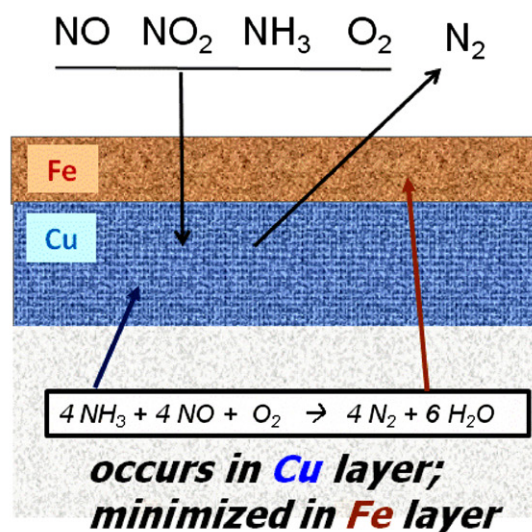
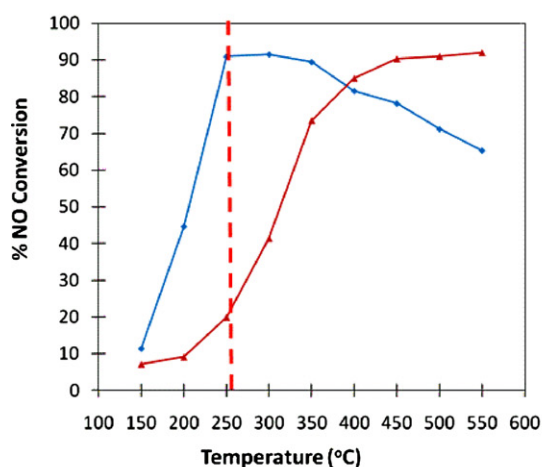


Fig. 13. Approach used for the EDS analysis of elemental composition in dual layer washcoated catalysts.

(A) Low temperature operation



(B) High temperature operation

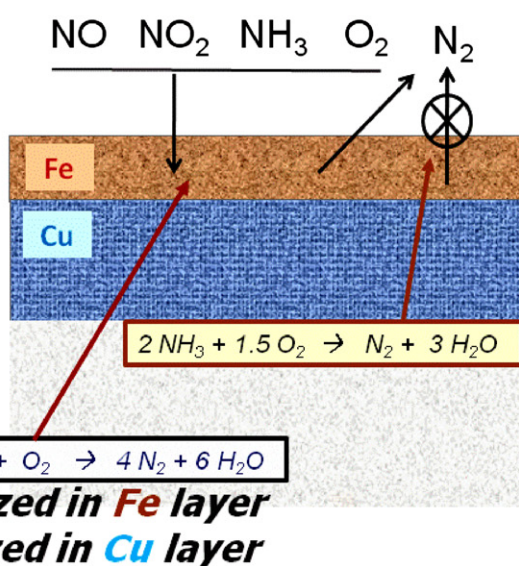
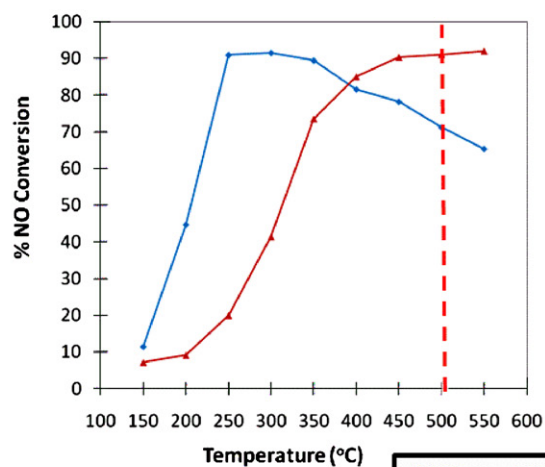


Fig. 14. Schematic of the working principle of the dual-layer SCR catalyst (A) low temperature; (B) high temperature.

proceeds at a much higher rate on the Cu-zeolite while NO_x reduction is more effective on Fe-zeolite. The steady state experiments carried out on different lengths and thicknesses of the Fe-zeolite catalyst defined the space velocity and loading needed to achieve a high NO_x conversion. As long as the thickness of the top Fe-zeolite layer is sufficient, most of the desired NO_x conversion should occur in the top Fe layer with the underlying Cu layer serving as a spectator. Thus at high temperature, reacting species encounter the SCR-active Fe layer first and reduction proceeds, unlike at lower temperatures in which it served as a comparatively inactive diffusion barrier.

Our approach of combining the Fe and Cu SCR catalysts in either a sequential brick arrangement or a dual layer system capitalizes on the differences in the kinetics of the desired (SCR) and undesired (ammonia oxidation) reactions over a wide range of temperatures. The results clearly demonstrate that there exists an optimum catalyst design that maximizes the NO_x conversion over a range of temperatures. In order to compute this maximum, the simplest model would need to include flow and reaction processes.

Only a few literature studies have reported the kinetics of standard and fast SCR reaction systems on Cu- and Fe-zeolite catalysts. Komatsu et al. [9] reported the kinetics of the standard SCR reaction on Cu-zeolite catalysts, suggesting the following power law kinetic model:

$$R_{\text{Cu-SCR}} = k_{\text{Cu}}[\text{NO}]^1[\text{O}_2]^{0.5}[\text{NH}_3]^0 \quad (6)$$

where k_{Cu} is the rate constant. In our recent study [11], we proposed the following power-law kinetics for the standard SCR reaction on Fe-zeolite catalysts:

$$R_{\text{Fe-SCR}} = k_{\text{Fe}}[\text{NO}]^1[\text{O}_2]^{0.55}[\text{NH}_3]^{-0.3} \quad (7)$$

where k_{Fe} is the rate constant. A few other literature studies [17,18] showed that the NH₃ oxidation reaction has a linear dependence on the NH₃ concentration. Since O₂ is present in excess in the feed, the following simple rate expression can be used to describe NH₃ oxidation reaction on Fe- and Cu-zeolite catalysts

$$R_{\text{NH}_3\text{-oxi}} = k_{\text{oxi}}[\text{NH}_3] \quad (8)$$

Our experimental results showed a difference in NH₃ oxidation activities on Fe- and Cu-zeolite catalysts. Thus the above rate expression with different values of rate parameters (k_{oxi}) should do a reasonable job of predicting the trends in the experimental data. As observed, there is a difference in the rates and selectivities of the standard SCR and NH₃ oxidation reactions for the Fe- and Cu-zeolite catalysts. These power law kinetic rate expression incorporated into a standard two-phase monolith model should be a good starting point to conduct an optimization study of the sequential brick configuration. However, for the optimal dual layer catalyst configuration, a two dimensional two phase model would clearly be required along with the detailed kinetics of all the above reactions. This complementary modeling work is the focus of ongoing research in our group and will be presented in a future publication.

3.10. Dual layer catalyst versus series arrangement of catalyst bricks

The above findings (Fig. 9) with the dual-layer catalyst resemble closely the results with the sequential Fe-Z/Cu-Z monolith configuration. A question of practical importance is which configuration is superior for a fixed mass of Cu- and Fe-zeolite. The dual-layer configuration spreads a prescribed amount (mass) of each catalyst over the entire length of the monolith. The series configuration concentrates the individual components over shorter lengths, necessarily resulting in thicker washcoats. Obviously, the contacting patterns of the reacting gas with the catalysts are different for the

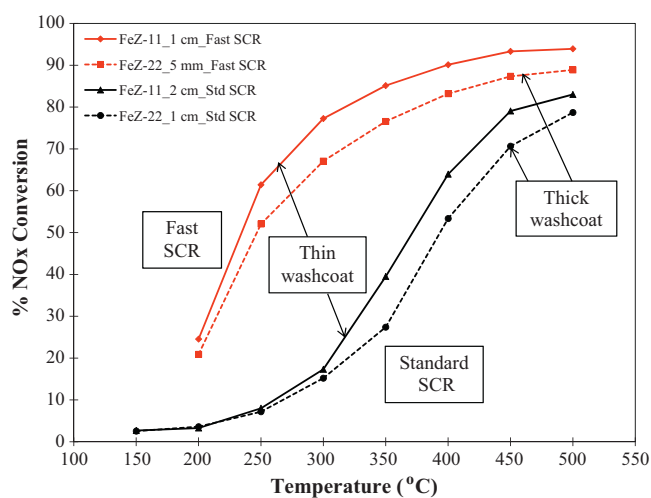


Fig. 15. Data showing the extent of transport limitations for standard and fast SCR reactions on in-house synthesized Fe-zeolite catalysts.

two configurations. The flow configuration and catalyst geometry directly impact the effectiveness of the transport of reactants to the catalyst sites via external mass transport and washcoat (pore) diffusion. Intuitively, if the reactions are purely kinetically limited, then there will be no effect of the transport processes and the overall conversion would simply be a function of the residence time of the flowing gas at the prescribed temperature. On the other hand, if either or both mass transport processes limit the reaction rates at least in part, then the overall conversion will obviously depend on the catalyst configuration. Thus, to answer the design question we must consider the effect of transport processes on the SCR reaction.

For this purpose, we synthesized catalysts with same washcoat volume and various washcoat thicknesses. Experiments were designed in such a way that the W/F ratio (mass of a catalyst/molar flow rate), i.e. the space velocity per unit mass of the catalyst remained the same in all the experiments [11,34]. This was achieved using different lengths of catalysts having varied washcoat loadings. For example, we used 2 cm length of FeZ-11 and 1 cm length of FeZ-22 catalysts for the standard SCR reaction. The same catalysts were used to study the presence of mass transfer limitations in the fast SCR reaction but with shorter catalyst lengths as the fast SCR reaction rates are very high. We used 1 cm piece of FeZ-11 and 5 mm piece of FeZ-22 catalysts for those experiments. The number of monolith channels was kept the same (28) for all the catalysts.

Fig. 15 shows typical results obtained for the standard and fast SCR reactions carried out on in-house synthesized Fe-zeolite catalysts. The results show separation in the NO conversion activity obtained on two catalysts with different washcoat thicknesses at higher temperatures (≥ 350 °C) for the standard SCR reaction. However the difference was negligible at lower temperatures. These results indicate the presence of washcoat diffusion (internal mass transfer) limitations for the standard SCR reaction on Fe-zeolite catalysts. This is because the reaction rates increase at higher temperatures for the standard SCR reaction because of which the entire catalyst (deep inside the thicker washcoat) is not utilized. Using a similar approach for the fast SCR reaction, we found that the difference in NO_x conversion activity studied on catalysts with different washcoat thicknesses emerged at temperatures lower than that for the standard SCR reaction. Our results showed a clear separation in NO_x conversion activities throughout the temperature range (200–500 °C). This confirms the presence of washcoat diffusion limitations for the fast SCR reaction in the Fe-zeolite catalyst over the

entire temperature range and the obvious reason of appearance of these diffusion limitations at earlier temperatures compared to the standard SCR reaction was very high reaction rates of the fast SCR reaction.

The presence of internal mass transfer limitations is an important issue for the above case of a series arrangement of bricks. Were we to use a small section of Fe-zeolite brick in front of a longer Cu-zeolite brick to improve the NO_x removal efficiency then diffusion limitations may inhibit the reaction in the front brick and most of the NH₃ and NO_x would be transferred to the downstream Cu-zeolite catalyst. This would result in a decreased NO_x conversion at higher temperatures. For this case, the dual layer catalyst system would have an advantage over the series arrangement of catalyst bricks.

We complete this study by making some final comments about the potential advantages of the dual layer catalyst system. The dual layer SCR catalyst has the advantage of high NO_x removal efficiency over a wider temperature range for standard SCR. The dual layer catalyst is especially useful for heavy-duty diesel engine vehicles as it provides the advantage of high NO_x reduction efficiencies at lower temperatures compared to Fe-only catalyst, as fraction of Fe-zeolite is replaced by Cu-zeolite. Also, at higher temperatures, very high NO_x reduction efficiencies could be achieved with higher SCR reaction rates in the top Fe-zeolite layer. This may reduce the need to have NO₂ in the feed, which would otherwise be needed to achieve high NO_x removal performance, especially at lower temperatures. Thus, indirectly at least, the dual layer catalyst reduces the need for the conversion of NO to NO₂ in the DOC unit, which is a potential savings in Pt needed to convert NO to NO₂ upstream. In addition, a recent study by Cavataio et al. [35] showed that contamination of the zeolite-based SCR catalysts can occur by precious metals like Pt, which travel from the DOC unit to the downstream SCR unit because of poor adhesion of Pt metals in the DOC washcoat. This results in a decline in the NO_x removal activity of SCR unit. With the dual layer SCR catalyst system, the DOC unit may be designed with reduced loadings of Pt which would prove to be cost effective and avoid the possible contamination of SCR unit by Pt. A final point to note is that the dual layer SCR unit may serve as a good NH₃ slip catalyst since it reduces the amount of unreacted NH₃ leaving the SCR unit. This is because both Fe and Cu are good ammonia oxidation catalysts and each selectively oxidize NH₃ to N₂. Few studies [13,18,20] focused on the optimum NH₃/NO_x ratio required to achieve high NO_x removal efficiency on Fe- and Cu-zeolite catalysts. For the Cu-zeolite catalysts, high NH₃/NO_x feed ratios are required at higher temperatures compared to Fe-zeolite catalysts because of the high NH₃ oxidation activity on the Cu catalyst. For the dual-layer catalyst system, the NH₃ requirement at higher temperatures may be decreased because of the increased standard SCR reaction rates on the Fe-zeolite catalyst present in the top layer. As a result, the optimum NH₃/NO_x ratio would decrease (compared to the Cu-only catalyst system) resulting in less consumption of NH₃ and hence less urea.

Amongst the different catalyst arrangement systems studied, the dual-layer catalyst system was found to give the highest NO_x removal efficiency. For this dual layer catalyst system, we used Fe-ZSM-5 and Cu-ZSM-5 catalysts. Even though the metal exchanged ZSM-5 catalysts give very high NO_x removal efficiencies, they are more prone to lose stability and hence NO_x removal efficiency at very high temperature (>700 °C) hydrothermal aging. Recently, various small pore zeolite catalysts like SAPO-34, SSZ-13, SSZ-16, etc. [29,30] have been introduced for the NH₃ SCR studies and were found to be highly stable towards very high temperature hydrothermal aging and highly efficient towards maximum NO_x reduction. The dual layer catalyst system design can be extended to these small pore zeolite catalysts to make this system more efficient.

4. Conclusions

A systematic study of standard and fast SCR reaction on combined Fe- and Cu-zeolite monolith catalysts was carried out to determine if a high NO_x conversion could be sustained over a wider temperature range than with individual Fe- and Cu-zeolite catalysts. To our knowledge, this is the first study introducing the concept of a novel dual-layer washcoated monolithic catalyst for widening the overall temperature window for the standard and fast SCR reactions.

Ammonia oxidation and standard SCR reactions were studied on individual Fe- and Cu-zeolite catalysts of different lengths to determine the activity of commercial and in-house synthesized Cu- and Fe-zeolite catalysts. In agreement with previous literature studies, the Cu-exchanged zeolite was found to be a very good low temperature (≤ 350 °C) NO_x reduction catalyst during the standard SCR reaction. Fe-zeolite was found to be a better NO_x reduction catalyst at higher temperatures (≥ 400 °C). A series combination of Fe-zeolite (in the front) (33–50% of the total length) followed by Cu-zeolite (50–67%) gave the highest NO_x conversion over a wide temperature range. The reverse series catalyst arrangement with the Cu-zeolite in front of the Fe-zeolite catalyst had little if any effect on the NO_x reduction efficiencies at higher temperatures. The results indicated that this catalyst system did not utilize the Fe-zeolite catalyst as the NO_x conversion activities were similar to the Cu-only catalyst system.

Standard and fast SCR experiments were carried out on various dual layer catalysts. Amongst the various combinations of dual-layered catalyst systems with Fe-zeolite catalyst layer on top of the Cu-zeolite catalyst layer, a catalyst with thinner (33% of the total washcoat loading) Fe-zeolite layer on top of a thicker (67% of the total washcoat loading) Cu-zeolite layer at bottom gave optimum NO_x reduction activities for both the standard and fast SCR reactions. The improvements in the NO_x conversion were obtained by exploiting the different reactivities of the two catalysts. At low temperatures the Fe-zeolite is relatively inactive compared to the Cu-zeolite, whereas at high temperatures the Fe-zeolite top layer is effective in converting most of the NO_x while minimizing the consumption of ammonia via its oxidation on Cu-zeolite. The dual layer catalyst results clearly indicate that an optimal dual-layer catalyst composition would maximize the NO_x conversion over a prescribed temperature range.

The dual layer Fe/Cu catalyst is shown to be a more effective configuration than the Fe/Cu series brick configuration because of the existence of washcoat diffusion limitations. The expansion of the temperature window is most notable for the standard SCR reaction, but performance improvement is obtained for fast SCR as well. The dual layer catalyst would be highly suitable for NO_x removal in heavy duty vehicles as it gives high NO_x reduction efficiencies over a wide temperature range. At high temperatures, it utilizes more selective Fe-zeolite top layer. While at lower temperatures, it utilizes highly active Cu-zeolite bottom layer which also reduces the requirements for feed NO₂ for Fe-only catalyst system. This would have the intangible benefit of reducing the precious metal requirements in the upstream diesel oxidation catalyst. Finally, comparison of fresh and hydrothermally aged catalysts indicates no noticeable reduction in catalyst performance.

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